

## An Ion Exchange Study of the Formation of Anionic Complexes in the Cupric and Cadmium Sulphate Systems

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The complex formation within the cupric and cadmium sulphate systems is investigated by determinations of the distribution of copper and cadmium between an anion exchanger, saturated with sulphate ions, and the complex solutions. It is found that at small total concentrations of the central ion a pronounced maximum in the distribution is obtained for a sulphate ion concentration of 50–70 mC.

It is proved that the only possible explanation of the maximum is a formation of anionic complexes at high ligand concentrations. The values of the distribution indicate on the other hand that the complexes are very weak. The results are combined with those from previous measurements, and it is shown that in all probability the systems are fairly "normal" and built up stepwise.

Cupric and cadmium sulphate solutions have been the subject of a great number of investigations with the aim of deciding which complexes are formed. Among investigations of the cupric sulphate system which are not based on the use of a neutral salt medium a spectrophotometric study by Näsänen<sup>1</sup> may be mentioned. In this it was assumed that only the first mononuclear complex can be formed, and though the validity of this assumption was not proved, the results show clearly that the complexity constant is greatly dependent upon the ionic strength. Thus, for a closer quantitative study of the composition of this system it seems necessary to use a neutral salt medium for maintaining the activity coefficients as constant as possible.

Two potentiometric investigations of this kind have been performed previously by the present author. In the first<sup>2</sup> of these a copper amalgam electrode was used, while in the second one<sup>3</sup> the method of ligand displacement was applied. The results indicate that the strength of the first two mononuclear complexes is slight, and consistent values of the first complexity constant were obtained. On the other hand, rather high and divergent values were calculated for the constant of the third complex. Thus it is probable that variations in the activity coefficients, influencing the two methods of measurement in

different ways, have not been sufficiently eliminated, and none of the high values of the third "constant" is reliable (*cf.* Fronæus<sup>2</sup>, p. 63).

Recently Leden<sup>4</sup> has carried out two investigations of the cadmium sulphate system, using a neutral salt medium. Measurements with an amalgam electrode gave results very similar to those mentioned above for the cupric sulphate system.

On the other hand, from measurements by means of a silver electrode and the silver sulphate system as an indicator it was concluded that only one complex (or ion pair) can be formed in the cadmium sulphate system. However, necessary corrections for the decrease in ionic strength by the complex formation were of the same magnitude as the emf differences measured. Furthermore, as the cadmium concentrations were not very low, the possibility of an influence upon the complexity constants of the silver sulphate system cannot be precluded.

Thus it seems to the present author that the different measurements reported do not give a satisfactory answer to the question of whether anionic complexes can be formed in the cupric and cadmium sulphate systems, and for that reason this question is taken up in the present paper. The investigation is performed according to a method developed in a previous work<sup>5</sup>. It is based upon the use of an anion exchanger saturated with the ligand (here  $\text{SO}_4^{2-}$ ), and though no quantitative calculations of complexity constants can be carried out, the method generally yields valuable information about the occurrence of anionic complexes.

#### THEORY OF THE METHOD

The equations that are used in the following but not deduced are to be found in the previous paper<sup>5</sup>. The central ion ( $\text{Cu}^{2+}$  or  $\text{Cd}^{2+}$ ) is denoted M and the sulphate ion A. An index R indicates the resin phase.

For the ratio  $\varphi$  between the total concentrations of the central ion in the exchanger phase,  $C_{\text{MR}}$ , and in the solution,  $C_{\text{M}}$ , we have at equilibrium the relation

$$\varphi = l_1 \frac{\alpha_1}{\alpha_{1\text{R}}} \quad (1)$$

if we assume that the first, uncharged complex exists.  $l_1$  is the Nernst distribution coefficient of this complex, and  $\alpha_1$  and  $\alpha_{1\text{R}}$  denote the fractions  $[\text{MA}]/C_{\text{M}}$  and  $[\text{MA}]_{\text{R}}/C_{\text{MR}}$  respectively. In order to keep the ionic composition of the resin phase approximately constant it is necessary not to use a neutral salt medium, but then at increasing concentrations of sodium sulphate the activity coefficients of the different ionic species in the solution certainly vary considerably. Nevertheless, since  $l_1$  refers to an uncharged complex this quantity can be assumed to be approximately constant.

Furthermore, if A is the only ligand in the resin phase, or if it forms strong complexes with M, then for a given system  $\alpha_{1\text{R}}$  is also a constant, since  $[\text{A}]_{\text{R}}$  is constant, and the variation in  $\varphi$  at increasing  $[\text{A}]$ -values gives a measure of the corresponding variation in  $\alpha_1$ . In the present case we know in advance that A forms only weak complexes. Then we should take into consideration that the anion exchanger presumably contains fixed amine groups in small

concentrations in addition to the quaternary ammonium groups, and that these amine groups, which we will denote B, can form rather strong complexes with cupric and cadmium ions and thus are not displaced as ligands by A.

Then, if  $\beta$  denotes the complexity constant of MB and  $\beta_j$  that of  $MA_j$ , we have the following relation:

$$\alpha_{1R} = \frac{\beta_1 [A]_R}{1 + \beta [B]_R + \sum_{j=1}^N \beta_j [A]_R^j} \quad (2)$$

Now, since the total concentration of B is constant,  $[B]_R$  increases and  $\alpha_{1R}$  decreases at decreasing values of  $C_{MR}$ . Thus, at small central ion concentrations the variation of  $\varphi$  is *increased* by the presence of the amine groups, and this is very valuable in those cases where the absolute values of  $\varphi$  are small owing to slight formation of anionic complexes with A.

If only the first complex can be formed, then  $\alpha_1$  is a monotonously increasing function of  $[A]$ , even if varying activity coefficients cause a decrease in  $\beta_1$ . This is evident from the investigation by Näsänen<sup>1</sup>.

On the other hand, if anionic complexes can also be formed in the system, then a maximum in  $\alpha_1$  may appear at a certain  $[A]$ -value within the concentration range investigated. For approximately constant  $\beta_j$ -values the maximum corresponds to the value 1 of the ligand number (*cf.* Fronæus<sup>5</sup>). At higher ligand concentrations, when the formation of anionic complexes is appreciable,  $\alpha_1$  decreases. It should be emphasized that the appearance of such a maximum cannot be explained in any other way. In those cases when  $C_{MR}$  is considerable, the sorption in the interior of the resin phase predominates, and then eq. (1) certainly is applicable without any correction. Consequently a maximum in  $\varphi$  indicates that anionic complexes can be formed.

However, since in the present case the complexes are weak, an adsorption on the surface of the resin, caused, for instance, by the coordination of M and its sulphate complexes to fixed amine groups, should be taken into consideration. If the surface adsorption decreases at increasing  $[A]$ , it might be supposed that a combination of the two effects — the sorption in the interior and the surface adsorption — could produce a maximum in  $\varphi$ , even if only MA can be formed. Thus we will deduce a more correct expression for  $\varphi$  under the last-mentioned condition.

Then we may assume that the total concentration  $C_{MS}$  of the central ion adsorbed on the resin surface is a function of  $[M]$  and  $[MA]$  only. Denoting the values of  $\partial C_{MS}/\partial[M]$  and  $\partial C_{MS}/\partial[MA]$  at  $C_M = 0$  (*i.e.*,  $[M] = [MA] = 0$ ) by  $a_1$  and  $a_2$  respectively, we get:

$$\left(\frac{dC_{MS}}{d[M]}\right)_{C_M=0} = a_1 + a_2 \left(\frac{d[MA]}{d[M]}\right)_{C_M=0} \quad (3)$$

Furthermore we have the relations:

$$\left(\frac{dC_M}{d[M]}\right)_{C_M=0} = 1 + \beta_1 [A] ; \left(\frac{d[MA]}{d[M]}\right)_{C_M=0} = \beta_1 [A] \quad (4,5)$$

$$\lim_{C_M \rightarrow 0} \frac{C_{MS}}{C_M} = \left(\frac{dC_{MS}}{dC_M}\right)_{C_M=0} \quad (6)$$

By combination of the relations (3)—(6) the following expression is obtained:

$$\lim_{C_M \rightarrow 0} \frac{C_{MS}}{C_M} = \frac{a_1 + a_2 \beta_1 [A]}{1 + \beta_1 [A]} \quad (7)$$

Since the ratio of surface area and mass of the resin was constant at the measurements,  $C_{MS}$  and  $C_{MR}$  can be expressed in the same units. Then in the present case  $(C_{MR} - C_{MS})/C_M$  is equal to the right member of eq. (1), and we have the final relation:

$$\lim_{C_M \rightarrow 0} \varphi = \frac{a_1 + (a_2 + \alpha_{1R}^{-1} l_1) \beta_1 [A]}{1 + \beta_1 [A]} \quad (8)$$

As  $a_1$ ,  $a_2$ ,  $\alpha_{1R}$ , and  $l_1$  are independent of  $[A]$ , it is at once evident from (8) that if only the first complex can be formed, then  $\lim \varphi$  for  $C_M \rightarrow 0$  is always — like  $a_1$  — a monotonous function of  $[A]$ . Thus if  $\varphi$  is determined experimentally, and a distinct, relative maximum is obtained, which persists or becomes more pronounced at decreasing values of the parameter  $C_M$ , the only possible explanation is that at least one anionic complex is also formed.

## EXPERIMENTAL

*Chemicals used.* Stock solutions of radioactive cadmium perchlorate, containing some  $Cd^{115}$  (from A.E.R.E., Harwell, England), and cupric perchlorate were prepared according to the methods described in previous papers<sup>1,2</sup>.

Sodium sulphate of analytical grade was used for the preparation of a 1 C solution, the concentration of which was determined by percolating samples through a  $H^+$ -saturated cation exchanger column and titrating with sodium hydroxide.

The anion exchanger, containing fixed quaternary ammonium groups, was Amberlite IRA-400. It was converted into the sulphate form and air-dried.

*Measurements.* It was possible to perform the experimental determination of the function  $\varphi$  with higher accuracy in the measurements on the cadmium sulphate system than in the measurements on the cupric sulphate system, since a radioactive cadmium tracer was used. Consequently the former system was investigated more closely. The cadmium concentrations of the different solutions were obtained by measuring the beta activity on a fixed volume with a G-M tube for liquids, solutions of known cadmium concentrations being used to provide calibration curves.

A complex solution of the volume  $v$  and of the initial composition:  $C'_M$  mC  $Cd(ClO_4)_2$  +  $C'_A$  mC  $Na_2SO_4$  was shaken in a thermostat at  $20.0^\circ C$  with the air-dried exchanger of the mass  $m$ . The value of  $v \cdot m^{-1}$  was always constant ( $15.0 \text{ ml} \cdot g^{-1}$ ), and  $C'_M$  had a constant value in one and the same measurement series.

At equilibrium between the two phases the anion exchanger was carefully separated from the solution, and the cadmium concentration,  $C_M$ , of the latter was determined. Then it was found that the values of  $C'_M - C_M$  were rather small in comparison to  $C_M$

Table 1. Ion exchange measurements on the cadmium sulphate system.  
 $M = Cd^{2+}$ ;  $A = SO_4^{2-}$

$C'_M$ mC	$C_A$ mC	$C_M$ mC	$C_{MR} \cdot 10^3$ mmole $\cdot$ g $^{-1}$	$\varphi \cdot 10^3$ l $\cdot$ g $^{-1}$
1.10	1	1.02	1.20	1.18
	14	0.98	1.79	1.83
	28	0.98	1.76	1.80
	54	0.97	1.88	1.94
	129	0.99	1.58	1.60
	400	1.02	1.25	1.23
	800	1.03	1.01	0.98
10.4	10	9.7	10.8	1.11
	31	9.6	11.4	1.19
	52	9.6	12.2	1.27
	100	9.6	12.0	1.25
	199	9.7	9.8	1.01
	400	9.8	8.9	0.91
	800	9.9	7.1	0.72
20.7	21	19.7	14.9	0.76
	42	19.6	15.8	0.81
	63	19.5	17.3	0.89
	100	19.6	17.1	0.87
	201	19.6	15.8	0.81
	400	19.7	14.3	0.73
	800	20.0	11.1	0.56

(see Table 1), and thus  $C_{MR}$  could not be obtained with great accuracy from this difference. For that reason the exchanger was eluted twice, each time with a 2 C sodium perchlorate solution of the volume  $v$ . After this elution the resin showed practically no radioactivity. Then the cadmium concentrations of the eluates were determined, and denoting their sum by  $C'_M$ , we can calculate  $C_{MR}$  from the relation:  $C_{MR} = v \cdot m^{-1} \cdot C'_M$ .

Since the resin could not be washed before the elution (*cf.* Fronæus<sup>6</sup>), the  $C_{MR}$ -value obtained in this way includes a quantity caused by the outer solution adherent to the resin particles after the separation. But the ratio of surface area and mass of the resin being the same in all the measurements, the quantity mentioned is of the form  $k \cdot C_M$ , where  $k$  is a constant. Thus the  $\varphi$ -values calculated differ by a constant term  $k$  from the true  $\varphi$ -values, but this circumstance is of no importance for the study of the variation in  $\varphi$ .

By anion exchange between the two phases the perchlorate ions, initially present in small concentrations in the outer solutions, were nearly completely exchanged for an equivalent amount of sulphate ions, but the relative variation in the high value of  $[A]_R$  by this exchange is quite negligible. The sulphate concentrations  $C_A$  at equilibrium were then calculated from the approximate relation:  $C_A = C'_A + C_M$ .

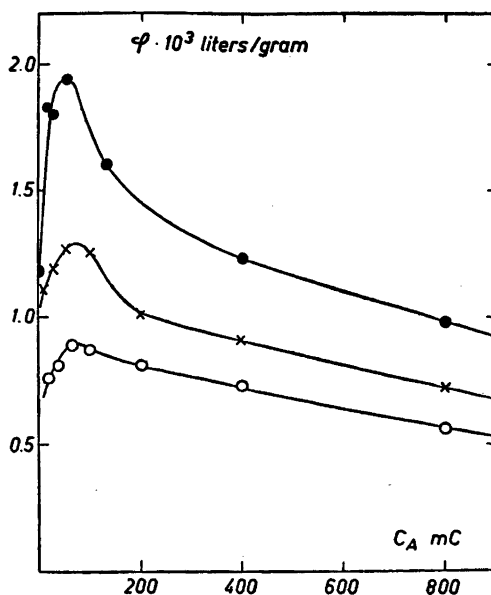


Fig. 1. The distribution  $\varphi$  as a function of  $C_A$  at different initial cadmium concentrations. 1.  $C'_M = 1.10$  mC ( $\bullet$ ); 2.  $C'_M = 10.4$  mC ( $\times$ ); 3.  $C'_M = 20.7$  mC ( $\circ$ ).

The data from the measurements on the cadmium sulphate system are collected in Table 1, and in Fig. 1  $\varphi$  is plotted against  $C_A$  with  $C'_M$  as a parameter.

It is seen that the  $\varphi$ -values increase considerably at decreasing values of the parameter and thus of  $C_{MR}$ . According to the theory given this fact can be explained by the presence of amine groups, to which the cadmium in the resin is preferably bound. Then for  $C_{BR} > C_{MR}$  we have  $[B]_R = C_{BR} - C_{MR}$ , and if eq.(1) is applicable, it is easily shown from eq.(1) and (2) that for a constant  $[A]$ -value  $\varphi$  should be a linearly decreasing function of  $C_{MR}$ . This is also found at higher  $C_A$ -values, e.g.  $C_A = 400$  mC, where we can put  $C_A \approx [A]$ .

For very small cadmium concentrations and at  $[A] = 50-70$  mC a pronounced maximum in the  $\varphi$ -curve is obtained, indicating that anionic complexes are also formed in appreciable amounts at higher sulphate concentrations.

In the investigation of the cupric sulphate system the method of measurement was the same, but the total cupric concentrations of the solutions were determined polarographically, after ammonia in excess and some gelatin had been added. The small cupric concentrations of the eluates could not be determined with very high accuracy, and for that reason only one measurement series with a low value of the parameter  $C'_M$  was carried out. The data obtained from the measurements on this system are to be found in Table 2, and the function  $\varphi$  is graphically represented in Fig. 2.

Table 2. Ion exchange measurements on the cupric sulphate system.  
 $M = Cu^{2+}$ ;  $A = SO_4^{2-}$

$C_M$ mC	$C_A$ mC	$C_M$ mC	$C_{MR} \cdot 10^3$ mmole $\cdot$ g $^{-1}$	$\varphi \cdot 10^3$ l $\cdot$ g $^{-1}$
1.67	2	1.61	0.93	0.58
	15	1.59	1.26	0.79
	28	1.58	1.33	0.84
	45	1.59	1.20	0.75
	60	1.59	1.15	0.72
	155	1.61	0.89	0.55
	300	1.62	0.78	0.48
	500	1.63	0.64	0.39

The  $\varphi$ -values are lower than the corresponding ones in the first measurement series on the cadmium sulphate system, though the difference in the  $C_M$ -values is rather small. The explanation could be a small amount of free perchloric acid in the cupric perchlorate preparation, lowering the values of  $C_{BR}$ ,  $a_1$ , and  $a_2$ . In any case the form of the  $\varphi$ -curve is very similar to that of the cadmium sulphate system, and no doubt the two systems are built up very analogously.

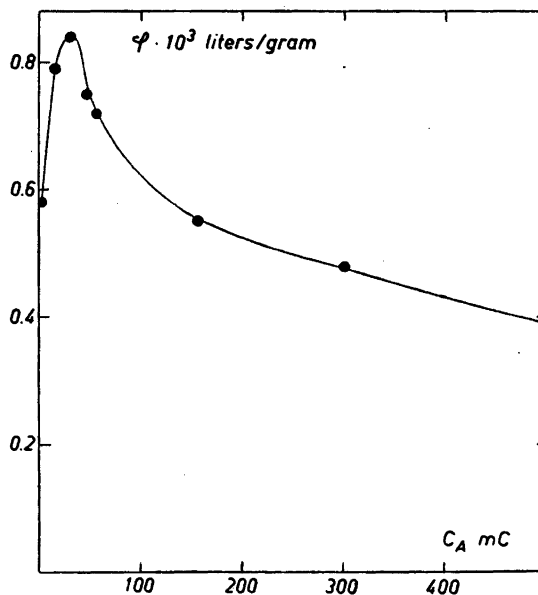


Fig. 2. The distribution  $\varphi$  as a function of  $C_A$  at the initial cupric concentration  $C_M = 1.67$  mC.

## DISCUSSION

There are two effects that we have not hitherto taken into consideration. At increasing sulphate concentration in the outer solution the amount of diffusible non-exchange electrolyte in the resin also increases, and furthermore a de-swelling of the resin takes place.

In the exchanger with a very high value of  $[A]_R$  and in the presence of the fixed amine groups the concentration  $[M]_R$  is certainly quite negligible, and then, if only the first complex can be formed, we have  $\alpha_{1R} \approx \beta_1[A]_R/(\beta[B]_R + \beta_1[A]_R)$ . Assuming  $[A]_R \geq 3 C$  for  $[A] = 0$ , we can calculate approximately by means of the Donnan equation that the increase in  $[A]_R$  due to the former effect is less than 7 % at  $[A] \leq 0.5 C$  and thus it cannot cause the pronounced maximum in the limit curve for  $\varphi$ .

On the other hand, since the ratio  $[A]_R/[B]_R$  is independent of the de-swelling, the latter effect cannot noticeably influence the  $\varphi$ -values.

Then the only possible explanation of the appearance of the pronounced maximum is a formation of anionic complexes within both systems. In the previous paper<sup>5</sup> it was shown, however, that the maximum value of  $\varphi$  is a qualitative measure of the strength of the anionic complexes, and thus from a comparison with the  $\varphi$ -curve for the cadmium bromide system<sup>5</sup> we conclude that the anionic complexes in the sulphate systems are very weak.

If these results are compared with the quantitative data from the measurements<sup>2,4</sup> with amalgam electrodes, we find that the values  $\beta_1 = 8-10 C^{-1}$  and  $\beta_2 = 10-17 C^{-2}$ , determined at the ionic strength 1 C for the cupric and 3 C for the cadmium sulphate system with sodium perchlorate as a neutral salt medium, seem very probable. On the other hand, the high values obtained of  $\beta_3$  (100 or 200  $C^{-3}$ ) are not supported by the present investigation. Consequently we must conclude that these sulphate systems are step systems with fairly "normal" values of the ratios between the stability constants  $b_j = \beta_j/\beta_{j-1}$  ( $\beta_0 = 1$ ) in a neutral salt medium. Here it should be mentioned that  $\varphi_{\max}$  is attained at lower  $[A]$ -values than those calculated from the values of  $\beta_1$  and  $\beta_2$  above. This can be explained by the fact that in the absence of sodium perchlorate the value<sup>1</sup> of  $\beta_1$  increases very much at decreasing sulphate concentration.

In the amalgam measurements the quantity determined is exactly  $(1 + \sum_{j=1}^N \beta_j [A]^j) f_M^0/f_M$ , where  $f_M^0$  denotes the value of the activity coefficient  $f_M$  for  $[A] = 0$ . From the investigation by Näsänen<sup>1</sup> we get for cupric sulphate  $\beta_1 \approx 4 C^{-1}$  at  $[A] = 1/3 C$ . Thus, if the ionic strength is kept constant at 1 C by means of sodium perchlorate, which is gradually exchanged for sodium sulphate, then  $\beta_1$  does not increase. Now, in  $\beta_1$  and  $\beta_2$  are included the quantities  $f_M f_A/f_{MA}$  and  $f_M f_A^2/f_{MA_2}$ , respectively. Since MA is uncharged and  $MA_2$  and A have an equal net charge,  $f_{MA}$  and  $f_A/f_{MA}$ , certainly can be treated as constants, and thus  $\beta_2$  should vary in the same direction as  $\beta_1$ . Then, since the amalgam measurements formally give a high value of  $\beta_3$ , though in view of the present results the term  $\beta_3[A]^3$  surely is negligible, it is evident that at greater exchanges of sodium perchlorate the factor  $f_M^0/f_M$  increases rapidly, making the calculated  $\beta_3$ -value illusory (cf. Leden<sup>4</sup>).



Finally it should be pointed out that the great changes in the extinction curve (Ref.<sup>2</sup>, p. 104) at wave lengths  $< 325 \text{ m}\mu$ , that take place when sodium sulphate is added to a cupric perchlorate solution, make it probable that MA and MA<sub>2</sub> are "true" complexes, in which the sulphate ions are coordinated directly to the central ion as in the crystal structure of  $\text{CuSO}_4 \cdot 5 \text{H}_2\text{O}$ , investigated by Beevers and Lipson<sup>7</sup>.

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